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AGING AND DEGRADATION OF POLYOLEFINS
I. PEROXIDE-INITIATED OXIDATIONS OF
ATACTIC POLYPROPYLENE

Etsuo Niki, et al

Stanford Research Institute

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I. Peroxide-Initiated Oxidations of Atactic Polypropylene

By: ETSUO NIKI, CHRISTIAN DECKER, and FRANK R. MAYO

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Multiple Sponsorship

STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.

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I

CONTENTS

This report completely replaces and extends Report No. 9. There
are numerous minor corrections but no major additions.

AGING AND DEGRADATION OF POLYOLEFINS. I.
PEROXIDE-INITIATED OXIDATIONS OF ATACTIC POLYPROPYLENE

1. OBJECTIVE

The immediate objective of this work is to determine the rates, products, and mechanisms of the peroxide-initiated oxidations of atactic polypropylene at 25-55°, where the primary products are stable. These results provide an improved foundation for studies of photoinitiated and thermally initiated oxidations.

2. SUMMARY AND CONCLUSIONS

This work started with the assumption that di-t-butylperoxy oxalate (DBPO) would provide a quantitative standard for polymer radical production in polypropylene (PP) and a calibration for initiation by ^{60}Co γ-initiation. Early experiments (Section 9.2.3) indicated that the t-BuO· groups not recovered as t-Bu$_2$O$_2$ or t-BuOH could be quantitatively identified as the polymer ether, t-BuOP, and we proceeded on the basis that t-BuOP could be determined by difference. Since the efficiency of radical production is the difference between the yields of t-BuOH and t-BuOP (Section 4), the efficiency is uncertain to at least 1 or 2%. This uncertainty is not important when the efficiencies are 10% or more, as in many oxidations, but is serious when the efficiency is only 1 or 2%, as it often is in the absence of oxygen. It now appears that combination of many radiation experiments[1] gives more accurate data than we can obtain with DBPO.

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(1) C. Decker and F. R. Mayo, γ-Initiated Oxidations of Atactic Polypropylene, Final Report (No. 11), on SRI Project 8012-1 (August 1972); Final Report (No. 9), SRI Project 8012-2 (August 1972).

In all our work with DBPO, experiments were carried out over
several half-lives of the initiator; thus, the stated results include
the effects of both the initial fast and the final slow radical produc-
tion. This work shows that the efficiency of polymer radical production
by DBPO is only 1 to 2% with solvent-free bulk polymer in the absence of
oxygen but is increased by retained or added solvents (Section 4). Most
of the PP· radicals thus produced apparently disproportionate to give PP
and unsaturated groups; little crosslinking occurs. A radical balance
in a concentrated o-dichlorobenzene solution is given in Figure 2.

In oxidations of PP dispersed on glass wool, efficiencies at 45^0
with a PP fraction of $\overline{M}_n$ = 10,650 range from 6 to 26% depending on the
proportion of DBPO used as initiator (Section 5.2). This trend is due
to the plasticizing effects of DBPO, its decomposition products, and the
resulting oxidation products. Therefore, to determine the effect of in-
creasing rate of initiation (different concentrations of DBPO) on the
rate and products of oxidation, it has been necessary to add an inert
diluent, di-t-butyl oxalate, and to compare results at the same efficiency
of initiation. It then appears that the efficiency of initiation, i.e.,
the ability of two t-BuO· radicals to avoid combination in the polymer
cage and to escape, is nearly inversely proportional to the rate con-
stant for chain termination by two PO_2· radicals (Section 5.2).

Our data on oxidation products and mechanisms (Section 6), are
consistent with our more precise data on γ-initiated oxidation.[1] Chain
propagation of PO_2· radicals gives only PO_2H groups; for present purposes
only tertiary C–H bonds are attacked. The rate of this reaction is half
order in [free PO_2·] radicals and on their rate of production. This re-
action can be completely inhibited by added antioxidant (Section 5.4).
The yields of PO_2H on O_2 absorbed and the kinetic chain lengths increase
with decreasing rate of chain initiation. In this report, the maximum

2

yield of PO_2H was 70% (100% of chain propagation), and the maximum kinetic chain length at 45° was about 5 per <u>average</u> initiating radical (see below).

About 34% of the interactions of two $PO_2\cdot$ radicals are immediately terminating to give a peroxide crosslink, P_2O_2, stable in the dark at ambient temperatures. The rest of these interactions are nonterminating and give two $PO\cdot$ radicals ($+ O_2$). About 65% of these $PO\cdot$ radicals abstract hydrogen from the polymer to give alcohol (POH) and more $P\cdot$ and then $PO_2\cdot$ radicals. The other 35% cleave to ketone and primary alkyl, which give primary alkylperoxy radicals, most of which then terminate with the predominating $t-PO_2\cdot$ radicals to give POH and aldehyde as termination products. The yields and proportions of all these products are practically independent of the rate of initiation (first order in chain initiation), are unaffected by added antioxidant (Section 5.4), and are apparently the same whether the interacting radicals are in the initiating cage or meet in solution. These products and the hydroperoxides discussed above account for more than 90% of the oxygen absorbed. All are primary products and fairly stable under our experimental conditions. Cleavage and crosslinking reactions nearly compensate, and about half of the chain terminations occur by each of the indicated routes. At low rates of initiation, some of the primary alkylperoxy radicals must propagate before they terminate, with the result that formation of part of the carbonyl groups is less than first order in initiation.

The antioxidant studies indicate that only a small proportion of the $PO_2\cdot$ radicals generated by initiating $t-BuO\cdot$ radicals escape immediate cage termination. Hence the chain lengths in propagation for the $PO_2\cdot$ radicals that escape the cage are several times those that are indicated above and in the tables (Section 5.4).

Rates of "thermal" oxidations of atactic PP are insignificant (Section 5.6); so are the effects of excess glass wool and excess oxygen

3

pressure (Section 5.5). The independence of oxygen pressure in the range 264 to 1100 torr shows that the efficiency of initiation is determined by the competition of PP and P$\cdot$ radicals for t-BuO$\cdot$, not by the competition of t-BuO$\cdot$ and O_2 for P$\cdot$ radicals. Although the data are not wholly consistent, both the efficiency of initiation and the rate of chain termination appear to increase together with decreasing molecular weight and viscosity of the polymer (Section 5.5), just as they do with increasing solvent with a polymer of constant molecular weight (Section 4).

Concentrations of $PO_2\cdot$ radicals were measured by electron spin resonance in DBPO-initiated oxidations of PP and found to be extraordinarily high, about 10^{-3} $\underline{M}$ (Section 7.1). From the rates of production of $PO_2\cdot$ radicals and the accompanying rates of oxidation, it is found that rates of chain propagation and chain termination are much smaller in PP than in the liquid model, 2,4-dimethylpentane. However, these effects on propagation and termination compensate so that the ratio $k_p/(2k_t)^{1/2}$ is about the same in the polymer as in the model. Similar esr measurements in the presence of an antioxidant show no peroxy radicals but radicals from the substituted phenol. From this and other work[1] we conclude that only $PO_2\cdot$ radicals outside the initiating cage are seen by esr (Section 7.2).

This report provides new perspective on some previous work and a better foundation for further basic and applied research on oxidation and aging of PP in the light and at elevated temperatures. These subjects are discussed in Section 8.

3.   BACKGROUND

A preceding Report No. 8 on Project 8012-1, dated January 20, 1970, summarized in tentative form our research on the oxidation of atactic polypropylene (PP) at the exhaustion of project funds. We have since had one year of assistance from Dr. Christian Decker (Section 10)

4

and also supplementary contracts from the Army Research Office (Durham) to support supervision and report preparation, materials and shop assistance for Dr. Decker, and some experiments by Mr. Harold Richardson.

Ideally, we would like to issue a final report that contains all our data on PP that are worth keeping and then to condense that report for publication, but we cannot afford this duplication in reports. Accordingly, the remainder of this report corresponds closely to our proposed publication on the DBFO-initiated oxidation of atactic PP. It contains the results of a few new experiments by Dr. Decker (Tables IV and VI in Section 5), details of revised analytical procedures (Section 9), and revised material balances on products and discussions of mechanisms (Section 6). Section 11 lists useful material from previous reports that are not incorporated in this report. Dr. Decker has carried out extensive experiments on ^{60}Co γ-initiated oxidations of atactic PP at 45°. These will be presented separately.[1] Work by Dr. Decker and Mr. Richardson on γ-initiated oxidations of polyethylenes and ethylene-propylene copolymers is presented as a final report[2] for the related Project 8012-2 and will be released after approval by the sponsors of that project. Work on photochemical reactions of atactic PP[3] (some already in Report No. 8) will be presented as a third part of the final report on this Project 8012-1.

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(2) C. Decker, F. R. Mayo, and H. Richardson, Polyethylene and Ethylene-Propylene Copolymers, Final Report (No. 10), SRI Project 8012-2 (August 1972).

(3) T. Mill, H. Richardson, and F. R. Mayo, Photodecompositions of Model Peroxides, Final Report (No. 12), SRI Project 8012-1 (August 1972).

4. DECOMPOSITIONS OF DBPO IN BULK PP IN THE ABSENCE OF OXYGEN

For our research on the oxidation of PP near ambient temperatures, a known rate of initiation ($P\cdot$ radical production) was required. We chose for this purpose di-t-butylperoxy oxalate (DBPO). This peroxide is easily prepared,[4] has a convenient half-life (43.5 min in atactic PP at 45°), and its decomposition products are easily determined.[5] The important reactions are (1)-(6) in Figure 1.

$$\text{t-BuOO}\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}\text{OO t-Bu} \xrightarrow{1} [2\text{t-BuO}\cdot]_{cage} + 2CO_2$$

$$[2\text{t-BuO}\cdot]_{cage} \xrightarrow[\text{combination}]{2\ cage} \text{t-Bu}_2O_2$$

$$[2\text{t-BuO}\cdot]_{cage} \xrightarrow[\text{diffusion}]{3} \text{t-BuO}\cdot(\text{free})$$

$$\text{t-BuOH} + P\cdot \xleftarrow[PP]{4} \text{t-BuO}\cdot(\text{free}) \xrightarrow{5} AcMe + Me\cdot$$

$$\text{t-BuOH} + P\cdot \xrightarrow{6} \text{t-BuOP}$$

FIGURE 1   DECOMPOSITION OF DBPO IN PP

Each decomposition (reaction 1) produces a pair of t-BuO· radicals in a cage of substrate molecules. Some t-BuO· radicals combine with each other before they can separate or react otherwise and produce t-Bu_2O_2 (reaction 2); this compound measures the radicals that are wasted and cannot produce free radicals available for crosslinking or initiation

(4) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, J. Amer. Chem. Soc., 82, 1762 (1960).

(5) R. Hiatt and T. G. Traylor, ibid., 87, 3766 (1955).

of oxidation chains (4). The t-BuO· radicals that escape from the solvent cage (reaction 3) may abstract hydrogen from surrounding solvent or polymer molecules (reaction 4), or they may cleave to acetone (AcMe) and Me· radicals (reaction 5). In the latter case, the Me· radicals abstract hydrogen and produce radicals on the substrate. Thus the t-BuOH + AcMe measure the radicals from DBPO that produce substrate radicals, but AcMe is an important product only in aromatic solvents. The previously reported yields of useful radicals range from 95% in mobile aliphatic solvents to as little as 4% in polypropylene.[6,7]

Table I shows the results of decomposing DBPO in PP (Fraction 11) at 45° under nitrogen. In Expts. 9, 11, and 15, DBPO was decomposed in substantially solvent-free bulk PP. Nearly every P· radical is scavenged by the adjacent t-BuO· radical, and the efficiency of P· radical production approaches zero (0.1-1.7%). With increasing proportions of n-pentane, yields of t-BuOH increase and yields of $t-Bu_2O_2$ decrease. Finally, when the PP contains 88% of its weight of added solvent, about 54% of the free t-BuO· radicals abstract hydrogen atoms and the efficiency of initiation rises to 43%. When the stated efficiencies are small differences between large numbers, they are not known accurately (Section 6.2).

The intrinsic viscosity and calculated molecular weight of PP show little or no change after reaction under nitrogen. The near absence of crosslinking may be due to very low efficiencies of both P· radical production under nitrogen and of crosslinking. From the change in the molecular weight and the number of P· radicals produced, we conclude that about 15% of P· radicals couple (crosslink) and the rest disproportionate, but this value is only approximate. The efficiency of combination

(6) F. R. Mayo, Preprints of Papers, ACS Division of Polymer Chemistry, 8 (1), 11 (1967).

(7) F. R. Mayo and K. C. Irwin, Polym. Eng. Sci., 9, 282 (1969).

Table I

DECOMPOSITION OF DBPO IN PP AT 45° UNDER NITROGEN

Experiment No.	9	11	15	19	20	21	24
PP, mg	427.8	410.3	423.2	408.3	409.0	411.6	287.9
DEPO, μmole	124.4	114.5	125.2	122.2	117.9	115.8	123.1
mole/kg PP	0.291	0.279	0.296	0.299	0.288	0.281	0.428
Glass wool, g	1.3905	1.3029	1.1428	0.8820	0.7896	0.8579	--
Pentane,[a] retained wt% on PP	2.0	1.6	--	4.6,3	14.5,10	55.8,40	87.7[b]
Reaction time, min	410	425	410	400	410	455	440
Products							
$t\text{-}Bu_2O_2$, μmole	95.4	94.0	99.7	76.7	76.7	32.5	42.9[c]
% of $t\text{-}BuO\cdot$	76.7	82.1	79.7	62.8	65.1	28.1	34.8[c]
$t\text{-}BuOH$, μmole	29.1	22.4	26.3	49.1	44.9	96.3	131.8
% of $t\text{-}BuO\cdot$	11.7	9.8	10.5	20.1	19.0	41.6	53.6
$t\text{-}BuOR$, μmole (by diff.)	28.9	18.6	24.7	41.9	37.5	70.3	27.4
% of $t\text{-}BuO\cdot$	11.6	8.1	9.8	17.1	15.2	30.3	11.1
Efficiency,%[d]	0.1	1.7	0.7	3.0	3.8	11.3	43.0
$[\eta]$[e]	0.194	0.195	0.191	0.194	0.194	0.200	0.248
$\bar{M}_n$[f]	10550	10650	10450	10550	10550	11000	14900

[a] The first number of a pair represents the retained solvent calculated from weight difference; the second numbers are corrected for evaporation of solvent originally contained in the polymer into the vapor space in the reaction vessel. [b] o-Dichlorobenzene was solvent in Expt. 24. [c] Also found, 1.2 μmole of acetone, 0.5%. [d] Efficiency of production of polymer radicals, 100% × (t-BuOH + Me_2CO – t-BuOR)/(total t-BuO·). [e] Intrinsic viscosity of PP after decomposition of DBPO, measured at 35° in benzene solution; initial $[\eta]$ = 0.195. [f] Number-average molecular weight of PP after decomposition of DBPO, calculated from intrinsic viscosity; initial $\bar{M}_n$ = 10650.

8

for t-butyl radicals is reported to be 0.13 to 0.30, nearly independent of temperature.[8] The efficiency of crosslinking of atactic PP by dicumyl peroxide at 150^0 is less than 10%.[9] The calculated and estimated fates of t-BuO· and PP· radicals in Expt. 24, containing o-dichlorobenzene, are summarized in Figure 2.
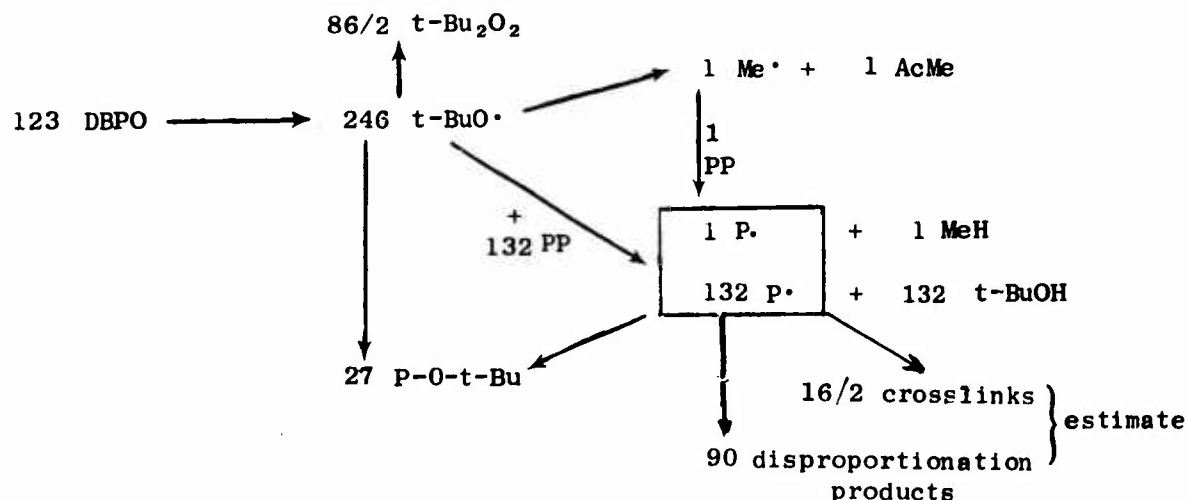
FIGURE 2   FATES OF t-BuO· AND P· RADICALS IN EXPERIMENT 24
(QUANTITIES IN μmoles)

5.   RATES OF DBPO-INITIATED OXIDATIONS OF ATACTIC PP

5.1.   Kinetics of Oxidation

The oxygen absorption by atactic PP at known rates of initiation is the sum of reactions that are half order and first order in rate of initiation. This sections lists these reactions and provides a basis for analysis, correlation, and interpretation of our data. It assumes that sufficient oxygen is present to convert all P· to PO_2· radicals (Section 5.5).

(8) J. O. Terry and J. G. Futrell, Can. J. Chem., 46, 664 (1968), and papers cited therein.

(9) A. E. Robinson, J. V. Marra, and L. O. Amberg, Ind. Eng. Chem., Product R and D, 1, 78 (1968).

Ideally, the net oxygen consumption in initiation and termination alone in the oxidation of atactic PP is equal to one-half the number of initiating radicals:

$$2 \text{ t-BuO} \cdot \ + 2 \text{ PP} \rightarrow 2 \text{ t-BuOH} + 2 \text{ P} \cdot \tag{7}$$

$$2 \text{ P} \cdot \ + 2 \text{ O}_2 \rightarrow 2 \text{ PO}_2 \cdot \tag{8}$$

$$2 \text{ PO}_2 \cdot \xrightarrow{k_t} \text{P}_2\text{O}_2 + \text{O}_2 \tag{9}$$

$$2 \text{ t-BuO} \cdot \ + 2 \text{ PP} + \text{O}_2 \rightarrow 2 \text{ t-BuOH} + \text{P}_2\text{O}_2 \tag{10}$$
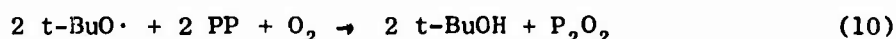
If some $PO_2 \cdot$ radicals are secondary, then they may terminate by $PO_2 \cdot$ + $P'-\overset{O_2}{\overset{|}{C}H}-P'' \rightarrow POH + P'-CO-P''$. Both kinds of termination can occur either in the polymer cage surrounding the initial radicals or between previously separated radicals. Accompanying these simple terminations is a more complicated one, approximating the reactions (11)-(14), and also having a close analog in the liquid-phase oxidation of isobutane:[10]

$$2 \text{ t-BuO} \cdot \ + 2 \text{ PP} + 2 \text{ O}_2 \rightarrow 2 \text{ t-BuOH} + 2 \text{ PO}_2 \cdot \tag{7,8}$$

$$2 \text{ PO}_2 \cdot /2 \rightarrow 2 \text{ PO} \cdot /2 + \text{O}_2/2 \tag{11}$$

$$\text{PO} \cdot \rightarrow R-\overset{O}{\overset{\|}{C}}-R' + R''-CH_2 \cdot \tag{12}$$

$$R''-CH_2 \cdot \ + O_2 \rightarrow R''-CH_2-O_2 \cdot \tag{13}$$

$$\text{PO}_2 \cdot \ + R''-CH_2O_2 \cdot \rightarrow POH + R''CHO + O_2 \tag{14}$$

$$2 \text{ t-BuO} \cdot \ + 2 \text{ PP} + 1.5O_2 \rightarrow 2 \text{ t-BuOH} + R-\overset{O}{\overset{\|}{C}}-R' + POH + R''CHO \tag{15}$$
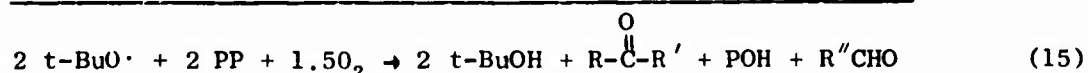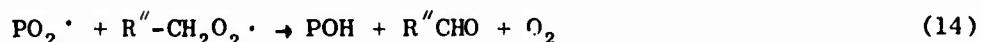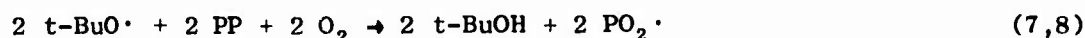
Since primary alkylperoxy radicals are about 10^4 times as reactive as tertiary alkylperoxy radicals in chain terminations,[11] we

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(10) D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, Adv. Chem. Series, 76, 40 (1968).

(11) K. U. Ingold, Accounts Chem. Res., 2, 1 (1969).

assume that most of the primary peroxy radicals formed in reactions (12) and (13) terminate by (14) instead of propagating. The terminating (9) and nonterminating (11) interactions of t-alkylperoxy radicals compete,[10] and (11) may also be followed by:

$$2PO_2 \cdot /2 \rightarrow 2\ PO \cdot /2 + O_2/2 \tag{11}$$

$$PO \cdot + PP + O_2 \rightarrow POH + PO_2 \cdot \tag{16}$$

$$PP + O_2/2 \rightarrow POH \tag{17}$$
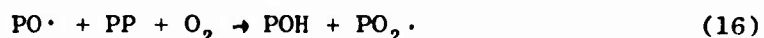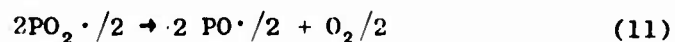
The above three sets of reactions, (7)-(17), are all first order in radicals and in rate of initiation (R_i). The relative rates of terminating and nonterminating interactions (9) and (11) and of cleavage and hydrogen abstraction reactions (12) and (16) should not depend on whether the 2 $PO_2 \cdot$ are initiated in the initial cage or diffuse together in the polymer. However, the net consumption of oxygen in these reactions that are first order in initiation will range from a minimum of one-half molecule of oxygen per initiating radical in reaction (10) to three-quarters of a molecule of oxugen in (15) and still more if reactions (11) and (16) are included.

Our experiments with added inhibitors (Section 5.4) and with γ-radiation[1] show conclusively that chain propagation and hydroperoxide formation result only from reactions of isolated percxy radicals, outside the initiating cage,

$$PO_2 \cdot + PP \xrightarrow{k_p} PO_2H + P \cdot \tag{18}$$

$$P \cdot + O_2 \rightarrow PO_2 \cdot \tag{8}$$

$$PP + O_2 \rightarrow PO_2H \tag{19}$$
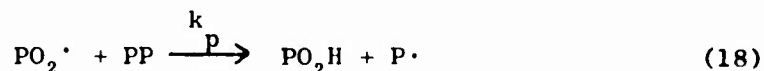
However, since the concentration of isolated $PO_2 \cdot$ radicals is proportional to the square root of their rate of formation (R_i) (and disappearance), the rate of chain propagation is half order in R_i. To a first

11

approximation, we assume that nearly all the attack on PP by either $PO_2\cdot$
(18) or t-BuO$\cdot$ radicals involves tertiary C-H bonds. An ordinary tertiary
aliphatic C-H bond is about 8 times as reactive as a sec-C-H bond toward
alkylperoxy radicals at 145°,[12] 15-20 times as reactive at 45°. In any
event, our analyses are inadequate to determine whether 10% of reactive
(14) involves sec-$PO_2\cdot$ instead of pri-$PO_2\cdot$ radicals.

The rate of oxygen absorption by the first-order reactions (10),
(15), and (17) is

$$-d[O_2]/dt = aR_i = 2\ aek_d[DBPO] \tag{20}$$

where $\underline{a}$ is a constant depending on the relative proportions of reactions
(10), (15), and (17), with a minimum value of 0.5 when (15) and (17) are
negligible, $\underline{e}$ is the efficiency of PP$\cdot$ radical production from DBPO, and
k_d is the first-order rate constant for decomposition of DBPO. For complete
decomposition of DBPO, the oxygen consumed in these reactions is

$$(\Delta O_2)_1 = 2\ ae[DBPO]_0 = a\ \Delta I \tag{21}$$

where ΔI is moles of initiating radicals.

The rate of oxygen absorption in chain propagation reactions (18)
and (8) at any time $\underline{t}$ during decomposition of DBPO is

$$-d[O_2]/dt = (R_i/2k_t)^{1/2}\ k_p[PP]$$

$$= k_p[PP](2ek_d[DBPO]_0 \exp(-k_d t/2k_t)^{1/2} \tag{22}$$

where R_i is the instantaneous rate of useful P$\cdot$ radical production and k_p
and k_t are defined by reactions (18) and (9), the latter complicated by
(14). The integration of equation (22) for complete decomposition of
DBPO ($t = \infty$) gives the O_2 absorbed in propagation:

(12) D. M. Brown and A. Fish, Proc. Roy. Soc. (London), A308,547
(1969). In 2,4-dimethylpentane, each tertiary H is about 9 times as re-
active as a secondary H toward t-BuO$\cdot$ radicals, T. Mill and D. Allara,
Paper No. 237 presented to Division of Physical Chemistry, 162 Meeting
of the American Chemical Society, September 1971.

$$(\Delta O_2)_p = 2(e[\text{DBPO}]_0/k_t k_d)^{1/2} k_p[\text{PP}] \tag{23}$$

The total oxygen absorption at complete decomposition of DBPO is

$$\begin{aligned}
(\Delta O_2)_{\text{abs}} &= (\Delta O_2)_1 + (\Delta O_2)_p \\
&= 2\,ae[\text{DBPO}]_0 + 2\,(e[\text{DBPO}]_0/k_t k_d)^{1/2} k_p[\text{PP}] \tag{24} \\
&= a(\Delta I) + b(\Delta I)^{1/2} \tag{25}
\end{aligned}$$

where $\underline{a}$ and $\underline{b}$ are constants, the former defined after equation (20). We define our kinetic chain lengths for non-cage propagation as

$$\text{kcl} = (\Delta O_2)_p/\Delta I = k_p[\text{PP}]/(e k_d k_t[\text{DBPO}]_0)^{1/2} \tag{26}$$

5.2.   Oxidation of PP at 45°

Results of oxidations of bulk PP in sealed tubes are summarized in Table II, where experiments are arranged in order of increasing DBPO concentration. The table shows the important effect of DBPO concentration on the efficiency of P· radical production, apparently due to a plasticizing effect. As the concentration of DBPO increases from 0.28 $\underline{M}$ to 2.7 $\underline{M}$, the yield of $t\text{-Bu}_2O_2$ decreases from 71 to 42% while the yield of t-BuOH increases from 18 to 36% and the efficiency of polymer radical production increases from 7 to 26%. At high DBPO concentrations, some acetone appears.

Comparison of Expt. 15 (which is very close to the average of Expts. 9 and 11 in Table I) with 25 and 28 in Table II shows that the efficiency of P· radical production is 6 to 7% under oxygen compared with 1% under nitrogen. Although this increase might be expected because reaction of P· radicals with oxygen should reduce ether formation (reaction 6) with geminate t-BuO· radicals, Section 5.5 shows that this explanation does not apply. Our best present explanation is that the accumulating PP oxidation products plasticize the PP and facilitate the escape of caged t-BuO· radicals.

13

Table II

DBPO-INITIATED OXIDATIONS OF PP ($\bar{M}_n$ = 10,650) at 45°

Experiment No.	25	28	31	29	16
PP, mg	410.7	433.9	432.2	344.5	214.3
DBPO, μmole	115.8	137.6	290.2	437.2	585.9
mole/kg PP	0.282	0.317	0.671	1.269	2.734
Glass wool, g	0.4875	0.2548	0.5505	0.4179	0.5253
Reaction time, min	360	380	450	400	410
Products from DBPO,% of t-BuO.					
t-Bu$_2$O$_2$	70.9	70.7	65.4	53.0	42.0
Me$_2$CO	0	0	0.8	2.8	6.3
t-BuOH	18.0	17.7	21.9	31.3	35.9
t-BuOR(by diff.)	11.1	11.6	11.9	12.9	15.8
Efficiency,%	6.9	6.1	10.8	21.2	26.4
$\Delta I = 2e$[DBPO], mole/kg PP		0.0387	0.145	0.538	
$(\Delta O_2)_{obs}$, mole/kg PP	not available	0.153	0.296	0.563	not available
$(\Delta O_2)_p^a$, mole/kg PP		0.128	0.203	0.218	
$(\Delta O_2)_p/\Delta I^b$ = kcl		3.31	1.40	0.41	
$(\Delta O_2)_p/(\Delta I)^{1/2 c}$		0.65	0.53	0.30	
$k_p/(2k_t)^{1/2} \times 10^4$		4.54	3.72	2.07	

[a] $(\Delta O_2)_p = (\Delta O_2)_{obs} - q\Delta I/2$ where q = 1.28.

[b] Average for all initiating radicals, not corrected.

[c] $(\Delta O_2)_p/(\Delta I)^{1/2} = k_p$ [PP]$(2/k_t k_d)^{1/2})$

14

Although Table II shows that the overall oxygen absorption $(\Delta O_2)_{obs}$ is closely proportional to $[DBPO]_0$ and also to $(\Delta I)^{1/2}$, we are most concerned with the oxygen absorbed in propagation, $(\Delta O_2)_p$, which differs significantly from ΔO_2 observed because the chain lengths are short (equation 24). The second and third lines from the bottom of Table II show that $(\Delta O_2)_p$ is not proportional to either ΔI or $(\Delta I)^{1/2}$ but appears to be proportional to $(\Delta I)^{0.2}$.

The following calculations show that $k_p/(2k_t)^{1/2}$ decreases slowly as $\underline{e}$ increases, probably because chain termination is faster in less viscous media. When values of $k_p/(2k_t)^{1/2}$ $(in^1/\underline{M}^{1/2}sec^{1/2})$ are calculated from equation (23), with $k_d = 2.74 \times 10^{-4}/sec$ (ref. 4 and Section 5.4), $\underline{e}$ is a fraction (not %), and $[PP] = 23.8$ moles/kg, these ratios decrease regularly from 0.00045 to 0.00020_7 as $\underline{e}$ increases from 0.061 to 0.21_2. To a good approximation, $k_p/(2k_t)^{1/2} = 0.00055 - 0.00161e$. This relation must fail at higher $[DBPO]_0$ since it predicts that $k_p/(2k_t)$ will equal zero at $\underline{e} = 0.34$. Experiment 46 (not listed) contained 943.5 mg PP-N, 1157 mg o-dichlorobenzene as solvent, and 0.192 mole DBPO/kg solution. The efficiency of initiation was 0.60 and the solution absorbed a total 0.246 mole O_2/kg, 0.099 in propagation. We calculate $k_p/(2k_t)^{1/2}$ to be 0.00032 (taking $\underline{M}$ and moles/kg to be equivalent), within the range of the experiments without solvent. All these calculations are based on the average radical generated, regardless of where it terminates.

On the premise that solvent effects on $\underline{e}$ and $k_p/(2k_t)^{1/2}$ are related, we carried out oxidations with an added inert ester, di-t-butyl oxalate (DBO), to compare the oxygen absorptions at different rates but similar efficiencies of initiation. Results are shown as Expts. 42 and 44 in Table III. For comparison, data for experiments A and B in Table III at the same efficiencies of initiation, without DBO, were interpolated from Expts. 31 and 29 in Table II. Solving

15

Table III

OXIDATIONS OF PP AT 45^0 WITH ADDED DBO

Experiment No.	42	A[a]	44	B[a]
PP, mg	434.2		427.0	
DBPO,μmole mole/kg PP	64.3 0.149	0.83_2[a]	135.0 0.316	1.00[a]
DBO,μmole mole/kg PP	400 0.921	0	482 1.129	0
Glass wool, mg	452.0		4?3.0	
Reaction time, min	400		400	
Products from DBPO,% of t-BuO·				
$t-Bu_2O_2$	64.0		52.3	
Me_2CO	0		0.8	
t-BuOH	24.8		31.4	
t-BuOR (by diff.)	11.2		15.5	
Efficiency,%	13.6	13.6	16.7	16.7
$\Delta I = 2e[DBPO]$, mole/kg PP	0.0405	0.226	0.106	0.335
$\Delta O_2)_{obs}$, mole/kg PP	0.119	0.368[b]	0.198	0.444[b]
$\underline{a}\Delta I$[c]	0.027	0.151	0.066	0.208
$\underline{b}\Delta I^{1/2}$[c]	0.092	0.217	0.13_2	0.236
$\underline{a}\Delta I/[\underline{a}\Delta I + \underline{b}(\Delta I)^{1/2}]$,%	23	41	33	47
$\underline{b}(\Delta I)^{1/2}/\Delta I = kcl$[d]	2.27	0.96	1.25	0.68

[a]   Interpolated from Expts. 31 and 29 in ⌐   ¬.

[b]   Calc. from $(\Delta O_2)_{obs}/[DBPO]_0 = 0.4_2$, which applies in both Expts. 29 and 31.

[c]   Calculated from equation (25) for each pair of experiments with the same $\underline{e}$.

[d]   Average propagations per initiating radical.

16

equation (25) for Expts. 42 and A gives $\underline{a}$ = 0.67 and $\underline{b}$ = 0.46. Simi-
larly, Expts. 44 and B give $\underline{a}$ = 0.62 and $\underline{b}$ = 0.41. Although there may
be a trend in $\underline{a}$ and $\underline{b}$ as $\underline{e}$ changes, these differences are insufficient
to establish one. For our calculations in Table II we used the mean
value, $\underline{a}$ = 0.64, which means that 0.28 O_2 is absorbed in reactions (15)
or (17) or both for each pair of terminating reactions, wherever they
may occur.

5.3.   Oxidations of PP at 25^0, 35^0, and 55^0

To study the effect of temperature on efficiency of initiation
and on the relative importance of the two kinetically different oxida-
tion processes, we also performed oxidations at 25^0, 35^0, and 55^0. The
probable activation energies for k_d, k_p, and k_t in reactions (1), (18),
and (9) suggest that the overall kinetic chain length should increase
with temperature in the cage oxidation but decrease in the non-cage
oxidation. Results are summarized in Table IV. The efficiencies of PP·
radical production increased from 1.4% at 25^0 to 15-21% at 55^0, probably
because of the decrease in PP viscosity with increasing temperature.
Table IV shows that, whereas the total oxygen absorption at $[DBPO]_0$ =
0.32 mole/kg increases slightly with temperature, the overall kinetic
chain length decreases with increasing temperature; the much higher
rate of radical production at 55^0 more than offsets the favorable effect
of temperature on $k_p/(2k_t)^{1/2}$. These results support the conclusion
that most of the oxygen absorption is associated with propagation of
free PO_2· radicals.

5.4.   Inhibited Oxidations of PP at 45^0

This section and Table V summarize our results of oxidizing PP
at 45^0 in the presence of about 0.34 mole DBPO/kg PP and increasing
proportions of 2,6-di-t-butyl-p-cresol, abbreviated here to QOH. A

17

Table IV

OXIDATIONS OF PP AT 25 TO 55°

Experiment No.	1[a]	36	28	34	35
Temperature, °C	25	35	45	55	55
PP, mg	320	318.9	433.9	433.9	226.4
DBPO, µmole	180	99.6	157.6	134.6	73.9
mole/kg PP	0.56	0.312	0.317	0.310	0.326
Glass wool, g	0.1538	0.3037	0.2548	0.4037	0.4210
Reaction time, min (hours)	(138)	1740	380	120	120
Products from DBPO, % of t-BuO·					
t-Bu$_2$O$_2$	62.8	74.1	70.7	67.3	68.8
Me$_2$CO	0	0	0	trace	1.0
t-BuOH	19.3	14.6	17.7	23.8	25.1
t-BuOR (by diff)	17.9	11.3	11.6	8.9	5.1
Efficiency, %	1.4	3.3	6.1	14.9	21.0
$\Delta I = 2e$[DBPO], mole/kg PP	0.0157	0.0206	0.0387	0.0924	0.137
ΔO_2, mole/kg PP	0.12	0.108	0.153	0.159	0.138
$\Delta O_2 / \Delta I$	7.6	5.27	3.95	1.72	1.01
$k_p / (2k_t)^{1/2} \times 10^4$	1.5	2.4	4.54	5.6	

[a] $\overline{M}_n = 13,800$; additional data in Table VIII.

18

Table V

DBPO-INITIATED OXIDATIONS OF PP WITH Di-t-BUTYL-p-CRESOL (QOH) at 45^0

(Concentrations in moles/kg PP)

Experiment No.		28	41	43	38
[DBPO]		0.317	0.340	0.317	0.320
QOH		0	0.0194	0.0391	0.141
t-Bu$_2$O$_2$	%	70.7	71.6	65.5	61.8
t-BuOH	of	17.7	17.2	22.1	22.7
t-BuOR, by difference	t-BuO·	11.6	11.2	12.4	15.6
$\underline{e}$, %		6.1	6.0[a]	9.7[a]	7.1[a]
$\Delta I = 2\underline{e}$[DBPO]		0.038	0.041	0.061	0.045
0.16 ΔI		0.006$_2$	0.006$_8$	0.010	0.007$_2$
$(\Delta O_2)_{obs}$		0.153	0.124	0.032	0.029
$\Delta O_2 - \Delta I/2$		0.134	0.103	0.0013	0.006
$(\Delta O_2 - \Delta I/2)\Delta I$		3.46	2.48	0.021	0.13

[a] Includes radical production from t-BuO· + QOH, offset by any reaction of t-BuO· with QO· (and, as usual, with PP·).

more thorough and conclusive study is reported elsewhere with γ-initiation;[1] it shows that QOH does not affect the cage oxidation, that it effectively stops all chain propagation (hydroperoxide formation), that each QOH destroys two PO$_2$· radicals, and that only 16% of the PP· radicals generated are normally able to propagate beyond cage restrictions (in the absence of any plasticizing effect of DBPO). This section shows that the experiments with both DBPO and QOH are consistent with the conclusions from γ-radiation studies but by themselves provide little quantitative information.

The conventional mechanism of inhibition[13] requires destruction of two peroxy radicals by one phenol and net absorption of one O_2 per initiating radical:

$$2 \; P\cdot \; + \; 2 \; O_2 \; \rightarrow \; 2 \; PO_2\cdot \qquad (8)$$

$$PO_2\cdot \; + \; QOH \; \rightarrow \; PO_2H \; + \; QO\cdot \qquad (27)$$

$$PO_2\cdot \; + \; QO\cdot \; \rightarrow \; PO_2Q{=}O \qquad (28)$$

Oxygen absorptions in Expts. 43 and 38 correspond within experimental error to those calculated on the principles above: $(\Delta O_2)_{obs} = 0.84a\Delta I/2 + 0.16 \; \Delta I$. The value of $\underline{a}$ from Table III is 1.28; for Expt. 43 it is calculated to be 0.85 for the stated $\underline{e}$, 1.33 if $\underline{e}$ is taken as a more representative value of 7%;[14] for Expt. 38, $\underline{a}$ is calculated to be 1.15. Although Expt. 41 contains several times the QOH needed to scavenge the 16% of the $PO_2\cdot$ radicals that escape the cage, the retardation is slight. This result apparently means (1) that more than 16% of the $PO_2\cdot$ radicals are escaping the cage in the DBPO + QOH experiment, or (2) that the $\underline{e}$ stated in Table V is too small, or (3) that some DBPO and QOH react directly with some waste of both. These factors are large enough to affect the calculated values of $\underline{a}$ in Expts. 43 and 38 but not its order of magnitude.

(13) E. C. Horswill, J. A. Howard, and K. U. Ingold, Can. J. Chem., <u>44</u>, 985 (1966).

(14) The $\underline{e}$ values in Table V appear to center on 6-7%. The 9.7% in Expt. 42 and the 2.2 and 1.9% in two omitted experiments apparently represent experimental errors.

5.5.　Effects of Excess Glass Wool, Oxygen Pressure, and Molecular Weight of PP

Data on the effects of the above variables on the oxidation of PP are summarized in Table VI. Experiments 54 and 53 show no significant effect of quantity of glass wool on efficiencies; the O_2 absorptions are not much different.

Experiments 28 and 49, where the initial oxygen pressures differ by a factor of 4.2, show that oxygen has little or no effect on the efficiency of initiation or rate of oxidation. When one of a pair of t-BuO· radicals has reacted with PP (reaction 7), we have in the immediate vicinity one remaining t-BuO· radical, one P· radical, O_2, and surrounding PP. Either of two sets of competing reactions may then determine the ratio of t-BuOH/t-BuOP formed. If the competition of the one P· radical for the one t-BuO· radical or for O_2 is important, the product ratio will be inversely proportional to the oxygen pressure. If the competition of the one t-BuO· radical for the one P· radical or for PP is important, the product ratio will be independent of oxygen pressure. Even though the yield of t-BuOH is suspiciously high in Expt. 49, the ratios of t-BuOH/t-BuOP in 28 and 49 are similar, 1.52 and 1.74, in spite of the fourfold change in oxygen pressure. The stated efficiencies in the table indicate more difference, but if we subtract 1.3% from the (too high) yield of t-BuOH and add it to the yield of ether in Expt. 49, then the t-BuOH/t-BuOP ratio becomes the same as in Expt. 28 and $\underline{e}$ becomes a more consistent 8.2%.

We conclude that uncertainties in determination of efficiencies are the principal factor affecting our experiments with different amounts of glass wool and oxygen, and we now consider the effects of molecular

Table VI

OXIDATION OF PP AT 45°: EFFECTS OF GLASS WOOL, MOLECULAR WEIGHT, AND OXYGEN PRESSURE

Experiment No.	54	53	28	49	48	2[a]	3[a]
PP fraction	14	14	11	11	1		
$\overline{M}_n$	2880	2880	10650	10650	35300	7300	41000
PP, mg	434.8	435.0	433.9	438.0	434.2		
DBPO, mole/kg PP	0.321	0.320	0.317	0.323	0.315	0.57	0.56
Glass wool, g	0.3692	1.2458	0.2348	0.3419	0.5178		
O_2, torr at 45°			264	1100			
Reaction time, min	380	400	380	410	400	400	420
Decomp. products of DBPO,[b] % of t-BuO·							
t-Bu_2O_2	55.4	60.3	70.7	60.2	76.6	69	77.8
t-BuOH	28.2	24.5	17.7	25.3	13.7	20.9	17.6
t-BuOP (by diff.)	16.4	15.2	11.6	14.5	9.7	10.1	4.6
Efficiency, %	11.8	9.3	6.1	10.8	4.0	10.8	13.0
$(\Delta O_2)_{obs}$, mole/kg PP	0.171	0.161	0.153	0.165	0.154	0.323	0.193
$\Delta I = 2e\,[DEPO]_o$	0.076	0.060	0.039	0.070	0.025	0.125	0.145
$(\Delta O_2)_{obs}/\Delta I$	2.25	2.7	3.9	2.4	6.2	2.6	1.3
$(\Delta O_2)_p = (\Delta O_2)_{obs}$ − 1.28 e $[DBPO]_o$	0.12_2	0.12_3	0.12_8	0.12_0	0.13_8	$0.24_3^{\ a}$	$0.10_0^{\ a}$

[a] Additional data are in Table VIII.

[b] No appreciable amount of acetone was observed.

22

weight on efficiencies. With the exception of Expt. 49, the other six experiments in Table VI show a consistent increase in yield of $t-Bu_2O_2$ (55 to 78%) and fairly consistent decreases in yields of t-BuOH (28 to 14%) and t-BuOP (missing material, 16 to 5%) with increasing molecular weight of PP (2900 to 41,000). The last two decreases are a consequence of the increase in $t-Bu_2O_2$, which shows clearly that separat f 2 t-BuO· becomes more difficult in higher molecular weight polymers. 1   ˙ds of $t-Bu_2O_2$ are large enough and the trend is marked enough that it not obscured by experimental errors. However, the yields of t-BuOH and t-BuOP are smaller and more subject to experimental error, and the difference (e) between these less certain quantities is sufficiently erratic that the trend is not obvious.[15]

The values of $(\Delta O_2)_{obs}$ at 0.32 mole DBPO/kg PP in Table VI are independent of the molecular weight of the PP. Since the efficiency of initiation appears to decrease[15] with increasing molecular weight, $k_p/(2k_t)^{1/2}$ must increase correspondingly over the same range. This relation is now considered in more detail. If in equation (25) we take n, $[DBPO]_o$, k_d, k_p, and $[PP]$ as constant, the equation assumes the form $(\Delta O_2)_{obs} = me + n(e/k_t)^{1/2}$, where m and n are constants. Comparison of $(\Delta O_2)_{obs}$ and $(\Delta O_2)_p$ for Expts. 54, 53, 28, and 48, for which the e values appear to be most reliable[1,5] shows that the m term (the smaller one and the difference between the others) increases linearly with e while the larger n term increases only slightly with increasing molecular weight of the polymer. Thus the ability of 2 t-BuO· radicals to

---

(15) The following considerations suggest that e decreases from about 10% at $\overline{M}_n$ = 2900 to about 4% at $\overline{M}_n$ = 35,000. We neglect Expt. 28 (where the yield of $t-Bu_2O_2$ is unusually high and the yield of t-BuOH is unusually low compared with other experiments at $\overline{M}_n$ = 10,650, possibly due to crystallization of $DBPO^2$), and we allow that the efficiencies in Expts. 2 and 3 are too high because of the higher concentrations of DBPO used.

23

separate in initiation closely parallels the ability of 2 $PO_2 \cdot$ radicals to terminate. More precisely, our data show that $k_p(e/2k_t)^{1/2}$ is nearly independent of molecular weight, as suggested in Section 5.2.

5.6. Uncatalyzed Oxidations of PP at 45°

Table VII shows that the rate of oxidation of PP in the absence of DBPO and light is negligible compared with that in a DBPO-initiated oxidation (Expt. 28). Expt. 47 was carried out for about 10 half-lives of DBPO as in DBPO-initiated oxidations, but since the oxygen absorbed (2.1 μmoles measured by difference) was very small compared with initial oxygen (832.1 μmoles), Expt. 50 employed longer times. To test for auto-catalysis, oxygen was removed at the indicated intervals and measured with a toepler pump, and new oxygen was added to continue the oxidation. About the same rates of oxidation were observed as those in Expt. 47. Expt. 50 suggests that the thermal oxidation is not significantly auto-catalytic at 45°.

Table VII

UNCATALYZED OXIDATION OF PP IN THE DARK AT 45°

Experiment No.	47	50-1	50-2	50-3	28 (Table II) $\dfrac{0.317 \text{ mole DBPO}}{\text{kg PP}}$
Reaction time, hr Total	6.42	171	191 362	191 553	6.33
ΔO_2, mole/kg PP Total	0.007	0.137	0.212 0.349	0.181 0.530	0.153
R_o, mole/kg PP/hr	0.001	0.00080	0.0011 0.00096	0.00095 0.00096	0.0242

24

6. PRODUCTS OF DBPO-INITIATED OXIDATIONS OF ATACTIC PP

6.1. Proposed Mechanisms

For calculating material balances, the numbered reactions that we have proposed previously are organized into the scheme in Figure 3. This scheme starts with one effective initiating t-BuO· radical and enough PP units and O_2 molecules to account for our products. The small letters indicate the numbers of each kind of reaction (usually < 1 occurring per initiating radical). The products determined by analysis are in boxes; all are primary products. We have accounted for more than 90% of the oxygen absorbed; part of the missing oxygen may be in water and carbon oxides.[1]

$$\boxed{aPO_2H} \; + \; aPO_2\cdot$$

$$a \uparrow \; + \; O_2$$

$$18 \; + \; PP$$

$$(1+a+d)PP + t\text{-}BuO\cdot \; + \; O_2 \xrightarrow{7+8} (1+a+d)\,PO_2\cdot \qquad \boxed{fPOH} \; + \; \boxed{f\ \text{aldehyde}} \; + \; O_2$$

$$+ \; PO_2\cdot \qquad f$$

$$14$$

$$\boxed{\frac{b}{2}\,P_2O_2} \; + \; \frac{b}{2}\,O_2 \xleftarrow[9]{b} \quad \xrightarrow[11]{c} \quad \frac{c}{2}\,O_2 + cPO\cdot \xrightarrow{\frac{12}{13}} \boxed{f\ \text{ketone}} \; + \; fRO_2\cdot$$

$$d \Big| \begin{array}{c} +PP \\ +O_2 \end{array}$$

$$16$$

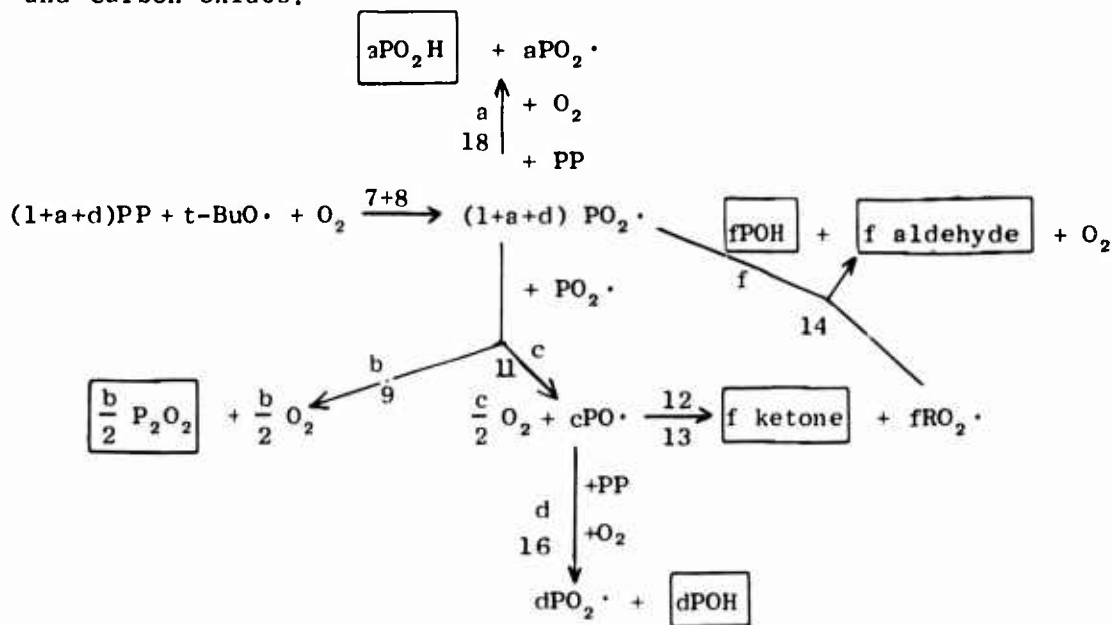$$dPO_2\cdot \; + \; \boxed{dPOH}$$

FIGURE 3 MECHANISM OF OXIDATION OF PP AT 25-45°

6.2. Correlation of Experimental Data

We have used the methods described in Section 9.3 to obtain product data in three experiments. Some data for these are already listed under Expts. 1, 2, and 3 in Tables IV and VI. Identifying and additional data appear in Table VIII.

25

Table VIII

OXIDATIONS OF ATACTIC PP INITIATED BY 0.56 M/kg PP DBPO

(Concentrations in moles/kg PP)

	Experiment No. (Temp.)		
	1 (25°)	2 (45°)	3 (45°)
$\overline{M}_n$ initial	13800	7300	41200
$\overline{M}_n$ oxidized	12400	7800	39500
Scission/kg PP	0.008	--	
Reaction time, hr	138	7	7
e, %	1.4	10.8	13.0
$\Delta I = 2e\,[DBPO]_0$	0.0157	0.123	0.146
ΔO_2	$0.12(100)^a$	$0.32_3(100)^a$	$0.19_3(100)^a$
PO_2H	0.085 (71)	$0.20_5(64)$	$0.10_1(52)$
P_2O_2	$0.00_6(5)$	0.04(12)	$0.03_7(19)$
$\supset C=O$	$0.01_4(6)$	0.05(8)	$0.06_2(16)$
POH	0.02(8)	0.07(11)	$0.03_5(9)$
Total, %	(90)	(95)	(96)
$PO_2H/\Delta I^b$	5.4	1.7	0.6_9
$(\Delta O_2 - PO_2H)/\Delta I^c$	2.2_4	0.96	0.63

		Experiment Number		
		1	2	3
	a	5.4	1.7	0.69
	b	0.76	0.65	0.51
	c	1.27	0.57	0.24
	d	0.82	0.37	0.028
	f	0.45	0.20	0.21
	b calc^d	0.11	0.59	0.58
	ΔI calc^e	0.026	0.13	0.14
	$(\Delta O_2\ calc)/\Delta I^f$	6.9	2.5	1.3
	$b/(b+c)^g$	0.37	0.53	0.68
	f/c^h	0.35	0.36	0.88
	$2f/(b+2f)^i$	0.54	0.38	0.46

[a] Numbers in parentheses are % ΔO_2 accounted for in designated products.

[b] $PO_2H/\Delta I = (\Delta O_2)_p/\Delta I$ = kinetic chain length.

[c] O_2 absorbed in reactions that are first order in initiator.

[d] b calc = 1 - 2f.

[e] ΔI calc = $2P_2O_2$ + carbonyl.

[f] $(\Delta O_2\ calc)/\Delta I = a + b/2 + d/2 + 3f/2$.

[g] Fraction of interactions of $PO_2\cdot$ radicals that is terminating.

[h] Fraction of $PO\cdot$ radicals that cleaves, also the fraction of total alcohol resulting from chain termination.

[i] Fraction of terminations involving $RO_2\cdot$ radicals from cleavage.

We now use the scheme in Figure 3 and the data in Table VIII to interpret Expt. 1. One initiating t-BuO· radical in Expt. 1 (0.0157 mole/kg PP) brings $1 + a + d = 7.22$ PP units (calculated) and 7.6 molecules of O_2 (0.12 mole/kg PP) into reaction as PO_2· radicals, in and out of the initiating cage. The additional a and d PO_2· radicals result from reactions (18) and (16). The $(1 + a + d)$ PO_2· radicals participating in the nonterminating interaction (11) is c, and the c PO· radicals react by either (12 or (16). We postulate that essentially all chain terminations occur by reactions (9) and (14), whose sum, b + 2f, should be 1 for each initiating t-BuO· radical. Both reactions are well established for oxidations of iso-butane[10] and cumene.[16] Since the average PO_2· radical propagates only about 7 steps before terminating and since primary peroxy radicals are 100 to 1000 times as reactive as tertiary peroxy radicals in chain termination,[11] we think that essentially all the f primary peroxy radicals formed by reactions (12) and (13) undergo termination with f more (mostly tertiary) PO_2· radicals. Thus, equal amounts of ketone and aldehyde should be formed. The molecules of products formed per initiating radical are then:

$$\text{aldehydes} = \text{ketones} = f \frac{C=O}{2\Delta I} = \frac{0.014}{2 \times 0.0157} = 0.445$$

$$\text{hydroperoxides} = a = \frac{0.085}{0.0157} = 5.4$$

$$\text{alcohols} = c = d + f = \frac{0.02}{0.0157} = 1.27, \text{ and } d = 0.82$$

$$\text{dialkyl peroxides} = \frac{0.006}{0.0157} = \frac{b}{2} = 0.38 \text{ and } b = 0.76$$

Since $b + 2f = 1$ and $2f = 0.89$, the fraction of terminations by b is 0.11 by difference ("b calc." in Table VIII), 0.76 by direct determination of P_2O_2, in which case f for aldehydes or ketones should be

(16) D. G. Hendry, J. Amer. Chem. Soc., 89, 5433 (1967).

only 0.12. These discrepancies in concentrations of P_2O_2 and $\geq C=O$ seem to be well beyond our experimental errors in determination of functional groups; they would be resolved if $e = 2.3\%$ instead of 1.4%, a difference within our probable error (see below).

The oxidation products account for net oxygen uptake per initiating radical as follows: $a + b/2 + d/2 + 3f/2 = 5.4 + 0.38 + 0.41 + 0.67 = 6.86$. Since the total molecules of oxygen absorbed is 7.6 per initiating radical, our estimated oxidation products account for 90% of the observed uptake. Considering the uncertainties in the infrared determination of carbonyl and alcohol groups, this agreement is within experimental error. The least certain value is e, the efficiency of initiation, determined by difference between two relatively large quantities. However, since e is in the denominator in calculations of a, b, c, d, and f, the relative values of these numbers are independent of e.

The data above show that of the 7.76 $PO_2\cdot$ radicals accounted for, 69.5% propagate by reaction (18) with PP 24.7% react with other $PO_2\cdot$, reactions (9) and (11), and 5.8% react with primary peroxy radicals formed by cleavage of alkoxy radicals. Of the 24.7% of $PO_2\cdot$ radicals that react with each other, only 34% appear to terminate; the other 66% give $PO\cdot$ radicals in nonterminating reactions. Of this 66%, 65% abstract hydrogen to give POH, and 35% cleave to ketone and primary alkyl radicals that eventually terminate with $PO_2\cdot$ radicals. Thus 54% of the termination is by route f, 46% by route b.

Experiment 3, using a new higher molecular weight PP is also included in Table VIII. This table shows that the efficiency of initiation increases sharply with a temperature increase from 25^0 to 45^0; the faster decomposition of DBPO[4] (half-life at $25^0 = 745$ min; at 45^0, half-life $= 42$ min) leads to shorter kinetic chains, smaller proportions of PO_2H formed in propagation, and larger proportions of termination products. With the higher molecular weight polymer at 45^0, the decrease in kinetic chain length is expected, because of the lower mobility of

28

free radicals in the medium, but the higher efficiency is not; however, it is within experimental error at this stage of our research.

Experiments 2 and 3 at 45°, with PP of higher and lower molecular weight (also in Table VIII), are now compared with Expt. 1, using the scheme in Figure 3. The discussion will point out the uncertainties in some of our data, particularly in the efficiency of initiation at 25° and in PCH formed, as well as some established semiquantitative conclusions.

At the higher temperature, as pointed out in Section 5.3, the efficiencies of initiation are higher (and therefore more accurately known) but the kinetic chain lengths are lower. Although the higher efficiencies of initiation at 45° are more accurately known and the values of b and b calc agree much better, Section 5.5 concluded that the experimental value of e is too high in Expt. 3.

We expected that the fraction of 2 $PO_2\cdot$ interactions that terminates, $b/(b+c)$, would decrease with increasing temperature as more pairs of $PO\cdot$ radicals escape from the polymer cage. However, the opposite trend is found in Expts. 1 to 3. This result could be due to a 1% error in the reported 1.4% efficiency of initiation in Expt. 1, which governs f and c; the yields of P_2O_2 ($= b/2$) have the expected trend.

Table VIII shows that there is usually a slight decrease in $\overline{M}_n$ during oxidation and that crosslinking (reaction b) approximately compensates for cleavage (reaction f). A gel permeation chromatogram on an oxidized sample of Fraction 13 ($\overline{M}_n = 6650$) showed that both crosslinking and cleavage do occur; the single, nearly symmetrical distribution peak before oxidation underwent a slight shift toward lower molecular weights and acquired a distinct high molecular weight shoulder. The normal effect of increasing temperature would increase the fraction of $PO\cdot$ radicals that cleave ($= f/c$). This trend is found in Expts. 1 and 3

29

but not in 1 and 2. However, Table VIII shows how sensitive this value is to changes in ΔI; both c and f are also sensitive to uncertainties in the ROH concentrations.

The last ratio in Table VIII is the fraction of chain terminations involving a primary $RO_2\cdot$ radical. All the ratios are rather similar and any trend is obscure.

The above discussion has stressed the uncertainties in our data and the discrepancies among experiments. However, our data do establish some new and semiquantitative conclusions, which are included in Section 2.

6.3.   Changes in Infrared Absorption

The infrared absorptions of PP were investigated as 22% solutions in CS_2 in an 0.093-mm cell. Typical absorptions of CS_2 alone, the original PP solution, and PP treated with DBPO at 45^0 under nitrogen and oxygen are shown in Figure 4. The decomposition of DBPO under nitrogen gives new absorptions at 1260/cm   (ether, t-BuOP?), 110C, 1020, 890 (vinylidene?), and 805/cm   (-CH=CH-?). Oxidized PP gives other new bands at 3300 (H-bonded HO and HO_2 groups) and 1720/cm   (carbonyl), but the absorptions underlined above diminished or disappeared; they apparently correspond to disproportionation products of P· radicals. The carbonyl absorption at 1720/cm   is sharp, and no appreciable absorption at 1785 (peracid[17]), 1780 (γ-lactone[18]), 1762 (perester[17-19]), 1745 (ester[17-19]), and 1710/cm   (acid[17-19])   could be detected.

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(17) J. D. Carlsson and D. M. Wiles, Macromolecules, 2, 587, 597 (1969).

(18) J. H. Adams, J. Polym. Sci. A-1, 8, 1077 (1970).

(19) J. P. Luongo, ibid., 42, 139 (1960).

30
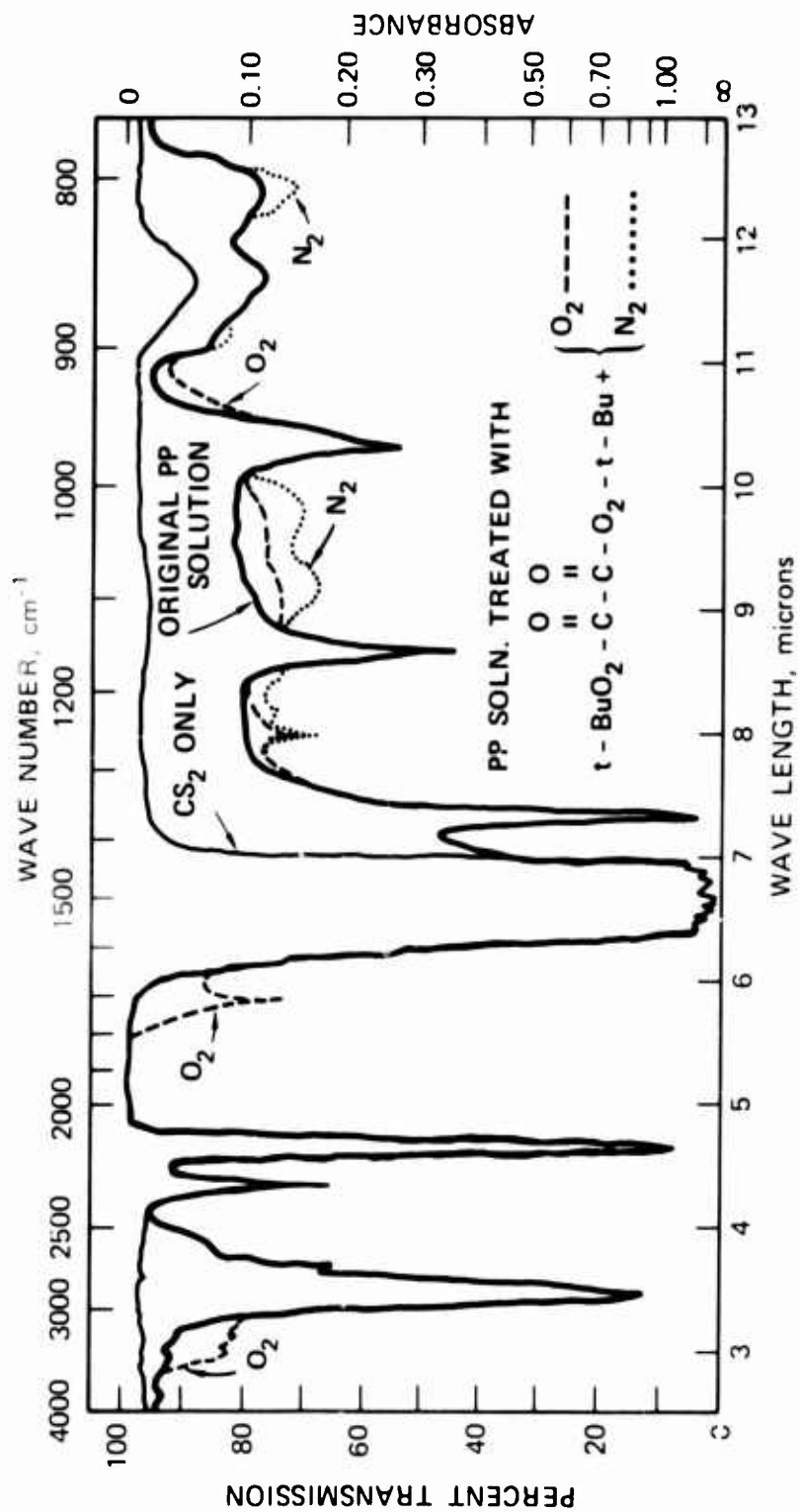
FIGURE 4   INFRARED ABSORPTION SPECTRA OF ATACTIC PP IN CS_2 IN 0.093-mm CELL

TA-320524-3

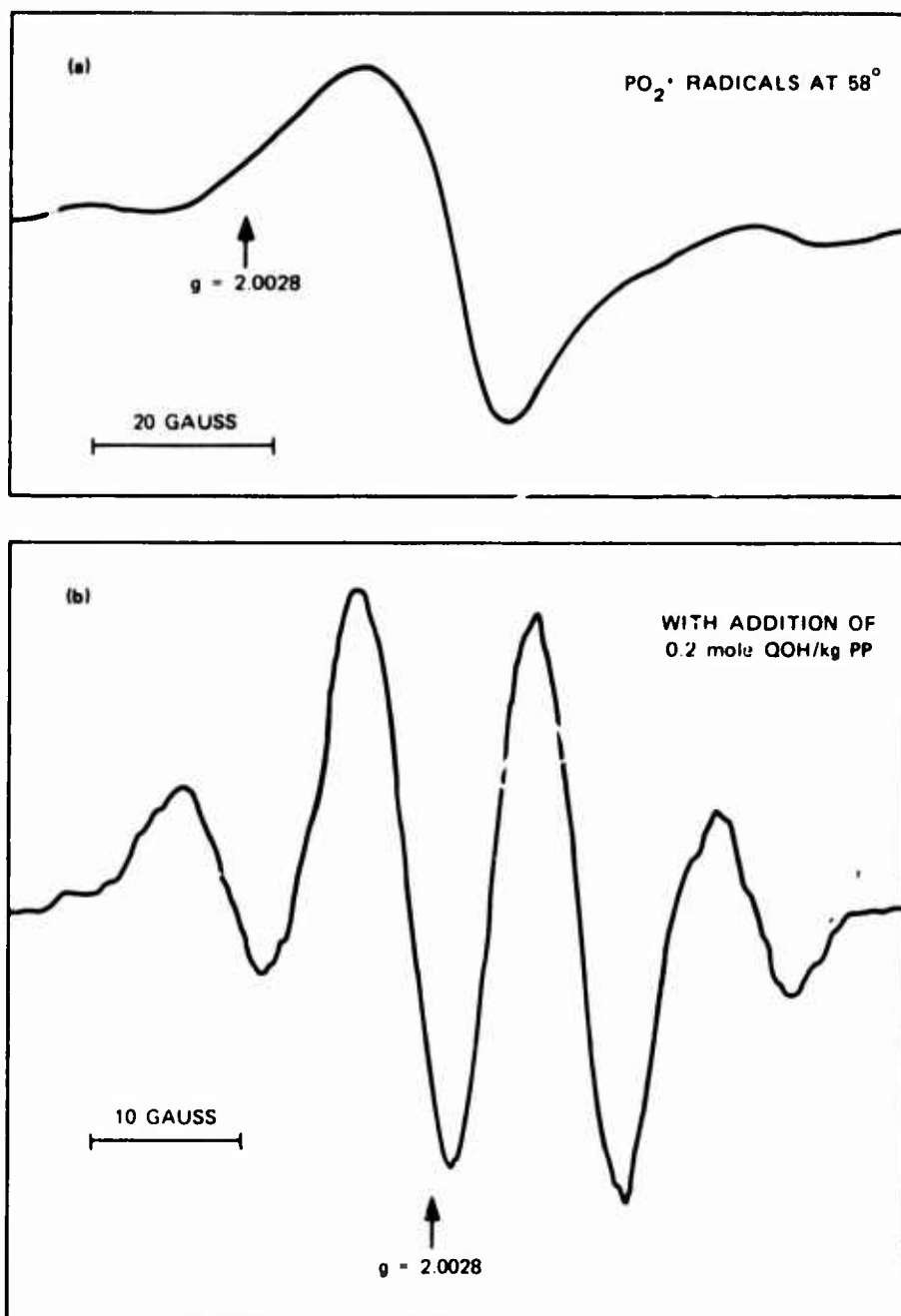7.   ESR STUDY OF DBPO-INITIATED OXIDATIONS OF ATACTIC PP

To confirm that peroxy radicals are present during oxidations
of PP and to determine their concentrations, we investigated the DBPO-
initiated oxidation of atactic PP at 45-63° ' means of esr spectros-
copy. Radical concentrations were too low for convenient measurement
at lower temperatures.

Sealed tubes containing PP + DBPO on quartz wool and one atmos-
phere of pure oxygen were introduced into a preheated esr cavity of a
Varian spectrometer (Model 4502). The temperatures in the cavity next
to the samples were measured by a thermocouple and spectra were recorded
after the samples reached constant temperature. The **g** values of the
radicals were calculated using the **g** value for standard pitch as 2.0028,
indicated by arrows in Figure 5. The radical concentrations were cal-
culated by integrating the first derivative signals and comparing them
with that of standard pitch.

7.1.   Uninhibited Oxidations of PP

As shown in Figure 5(a), the spectrum of oxidizing PP at 58°
consists of a broad symmetrical single line with no detectable hyperfine
structure; $g = 2.0259$ and the line width $\Delta w = 17$ gauss. We assign this
spectrum to $PO_2 \cdot$ radicals.

The signal reaches its maximum value after 2 minutes at 58° when
thermal equilibrium is attained, and then decreases according to a first-
order rate law (Figure 6). Spectra were recorded for 45°, 58°, and 63°.
Table IX shows that the half-life of $PO_2 \cdot$ radicals is about twice the
half-life of DBPO at these same temperatures. (When the $\lfloor DBPO \rfloor$ has de-
creased by three-quarters, $\lfloor PO_2 \cdot \rfloor$ has decreased by only one-half, and
so on.)

32

(a)

$PO_2 \cdot$ RADICALS AT 58°

$g = 2.0028$

20 GAUSS

(b)

WITH ADDITION OF
0.2 mole QOH/kg PP

10 GAUSS

$g = 2.0028$

TA-8012-17

FIGURE 5   ESR SPECTRA OF DBPO-INITIATED OXIDATIONS OF PP WITHOUT (a) AND
WITH (b) ADDITION OF QOH

Table IX

ERS STUDY OF DBPO-INITIATED OXIDATIONS OF PP

Temperature, ^{o}C	45°	58°	63°
$[DBPO]_0$, mole/kg PP	0.20	0.84	0.84
$[PO_2\cdot]$ x 10^4 after 2 min, mole/kg PP	1.5	10	14
Half-life $PO_2\cdot$, min	80	12.5	6.5
Half-life DBPO, min	43.5	7.5^a	4.0^a
Efficiency of initiation	0.061	0.3	0.48
k_t,[b] $\underline{M}^{-1}$ sec^{-1}	145	340	450
k_t,[c] $\underline{M}^{-1}$ sec^{-1}	23	55	72

[a]Ref. 4.

[b]By equation (30) in text.

[c]Corrected for escape from the cage of only 16% of the $PO_2\cdot$ radicals generated.

TA-8012-16
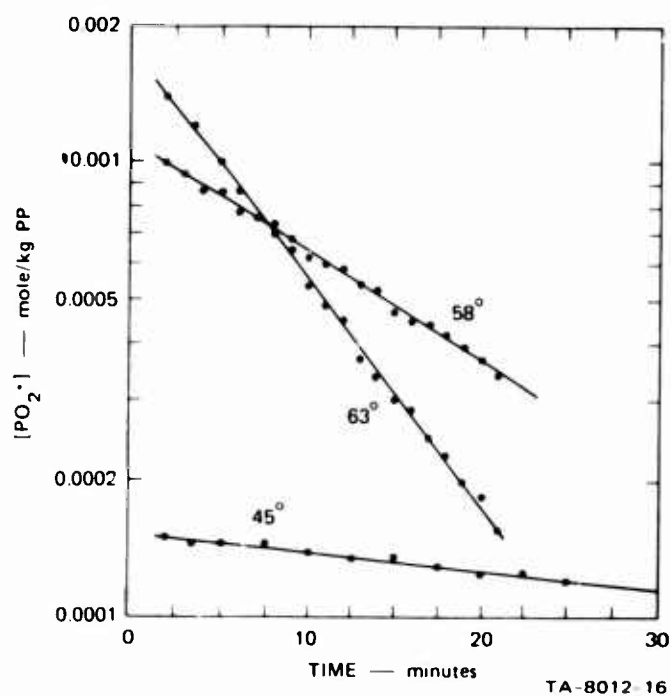
FIGURE 6   DECAY OF $PO_2\cdot$ RADICAL CONCENTRATIONS
AT 45 TO 63°

34

After 2 minutes at 58^0, the number of spins was calculated to be 7×10^{15} for one centimeter of column, which corresponds to a $PO_2 \cdot$ radical concentration of 10^{-3} mole/kg PP. This value allows us to determine the rate constant for statistical termination of $PO_2 \cdot$ radicals. The rate of initiation is:

$$R_i = 2ek_d[DBPO]_o \exp(-k_d t) = 2k_t[PO_2 \cdot]^2 \qquad (29)$$

Hence,

$$k_t = \frac{ek_d[DBPO]_o \exp(-k_d t)}{[PO_2 \cdot]^2} \qquad (30)$$

As shown in Table IX, the value of k_t increases from $145/\underline{M}$ sec at 45^0 to $450/\underline{M}$ sec at 63^0. The discussion below shows that k_t at 45^0 is 0.003 as large as that for 2-methyl-2-pentylperoxy radicals[20] ($k_t = 5 \times 10^4/\underline{M}$ sec at 45^0), mostly, but not entirely, because of a higher activation energy for k_t in the polymer. When we calculate the rate expression for k_t from the 45^0 and 63^0 experiments, $k_t = 10^{11.45} \exp(-13600/RT)$. However, the concentration of $PO_2 \cdot$ radicals in our experiment at 45^0 is too low and uncertain to give reliable values for A and E. From the 58^0 and 63^0 experiments alone, $k_t = 10^{10.7} \exp(-12400/RT)$.

When allowance is made for escape of a fraction of the $PO_2 \cdot$ radicals from the initial cage, the rate constants must be smaller. If we take this correction factor to be about 0.16 (the value we observed for γ-initiated oxidation of PP in the absence of any DBPO[1]), these rate constants k_t range from 23 to 72 $\underline{M}^{-1}$ sec. The calculated rate expression for k_t corrected for escape of 16% of the caged radicals becomes: $k_t = 10^{9.9} \exp(-12400/RT)$, which can be compared with the relation for 2-methyl-2-pentylperoxy radicals in 2-methylpentane solution, $k_t =$

(20) J. E. Bennett, D. M. Brown, and B. Mile, Trans. Faraday Soc., 66, 386 (1970).

$10^{11.1}$ exp(-9300/RT).[20] Thus, the low k_t for polymeric $PO_2\cdot$ radicals seems to be due to a low frequency factor as well as to a high activation energy.

Calculations of the ratio $k_p/(2k_t)^{1/2}$ at different temperatures (Table IV) enables us to evaluate k_p. Over the temperature range (25^0 to 55^0), $k_p/(2k_t)^{1/2}$ increases with increasing temperature according to the relation: $k_p/(2k_t)^{1/2} = 10^{2.7}$ exp(-9000/RT). The calculated value of k_p at 45^0 is then 0.0077/M sec. This value for all $PO_2\cdot$. radicals is about the same as that calculated for intermolecular propagation in 2,4-dimethylpentane at 45^0, 0.0075.[21] When our k_p is multiplied by $\sqrt{0.16} = 0.4$ to allow for $PO_2\cdot$ lost in the cage and Mill's value[21] is multiplied by 2 to include the accompanying intramolecular propagation, k_p appears to be one-fifth as large in PP (0.003) as in dimethylpentane (0.015). This result could be due to the low mobility of polymeric $PO_2\cdot$ radicals.

7.2.   Inhibited Oxidation of PP

Oxidations of PP were also carried out at 45^0 in presence of 0.2 mole/kg PP each of DBPO and 2-6-di-t-butyl-p-cresol (QOH). The resulting esr spectrum is shown in Figure 3(b); the quartet is attributed to a phenoxy radical. The expected hyperfine structure of four sets of triplets was not resolved.

The following considerations lead to the conclusion that our esr measurements of $PO_2\cdot$ radicals apply only to the 16% that escape first-order termination in the initiating cage. First, although most of the

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(21) T. Mill, private communication, based on work of G. Montorsi and T. Mill, Preprints, Division of Petroleum Chemistry, 16 (1), B23 (1971). The work of A. L. Buchachenko, K. Ya. Kaganskaya, M. B. Neiman, and A. A. Petrov, Kinetics and Catalysis, 2, 38 (1961) gives k_p = 0.11 for 2,3,6-trimethylheptane at 45^0. This result is suspect because E_p is found to be only 9.1 kcal/mole and E_t = 0.

36

$PO_2\cdot$ radicals originate and terminate as pairs in the cage, since their effective concentrations when formed are about 20 $\underline{M}$, they must disappear so rapidly that they make no measurable contribution to the steady concentration of $PO_2\cdot$ radicals. Second, the accompanying report[1] shows that sufficient QOH scavenges all the $PO_2\cdot$ radicals that escape the cage, but that excess QOH has no measurable effect on the cage reaction. Third, this section shows no evidence of $PO_2\cdot$ radicals in the presence of QOH.

Some additional ers experiments with atactic PP and DBPO in hexane solution are reported in Section 7 of Reference (1).

8. RELATION OF THIS WORK TO SOME PREVIOUS RESEARCH AND TO PRACTICAL PROBLEMS

Our good radical and product balances and the stabilities of our primary products at 25-55^0 provide an improved basis for correlating results of other coworkers at higher temperatures and in the light. We start with the paper of Tobolsky and coworkers,[22] which anticipates some of the principles we have presented, and with the papers of Van Sickle,[23,24] both of which are related to radical-initiated oxidations of PP.

Tobolsky et al.[22] oxidized films of bulk atactic PP with benzoyl peroxide as initiator, mostly at 95^0. They concluded that the oxidation has two components, one first order and the other half order in rate of initiation. Evolution of volatile materials prevented them from determining how much oxygen absorption is associated with the first-order reaction. Kinetic chain lengths were 4 to 18 for an assumed 60% efficiency of initiation by benzoyl peroxide. They studied chain cleavage by measuring stress relaxation in crosslinked films, found approximately one

(22) A. V. Tobolsky, P. M. Norling, N. H. Frick, and H. Yu, J. Amer. Chem. Soc., 86, 3925 (1964).

(23) D. E. Van Sickle, J. Polym. Sci. A-1, 10, 355 (1972).

(24) D. E. Van Sickle, J. Org. Chem., 37, 755 (1972).

cleavage per initiating (or terminating) pair of radicals, and deduced
(without product analyses) that cleavage occurs by our reactions (11)
and (12) and that termination involves primary $PO_2 \cdot$ radicals, like our
reaction (14). They probably missed some crosslinking by reaction (9)
to give P_2O_2, and they have no measure of POH formation by our reaction
(16). However, their work and ours together suggest that formation of
P_2O_2, although able to offset cleavage below 50^0, probably becomes less
important as $2PO_2 \cdot$ radicals separate more easily at higher temperatures
in a less viscous medium. The Tobolsky association of one cleavage with
one termination may be a good approximation under their experimental
conditions. However, at lower rates of chain initiation, particularly
under practical service conditions, we would expect that more primary
$PO_2 \cdot$ radicals would propagate instead of terminating and that the num-
ber of cleavages would then exceed the number of terminations. These
considerations suggest why accelerated aging tests are less than satis-
factory and how they might be improved (see also below).

Van Sickle[23] recently reported his studies of the $t-Bu_2O_2-$
initiated oxidation of PP in benzene solution under pressure, mostly
at 120^0. The paper deals mostly with rates and yields of hydroperoxides,
which never exceed 40% at 2% conversion and are lower at higher conver-
sions. No other major products were determined. This work shows the
need for product studies in interpreting results and the difficulties
introduced by secondary decompositions of hydroperoxides. Although a
separate experiment with oxidized PP shows that the peroxide content did
not decrease fast enough to account for the low yield of hydroperoxide,
it is not clear that this decomposition rate would apply in a $t-Bu_2O_2-$
initiated oxidation where the concentrations of radicals are higher and
where other and unknown products are being formed by reactions of other
chain carriers.

Van Sickle's recent report[24] on the t-BuO$_2$-initiated oxidation of 2,4,6-trimethylheptane at 100 and 120°, where most of the identified product was the trihydroperoxide, provides convincing evidence of a strong tendency for intramolecular propagation in the oxidation of PP. It also shows how interactions of neighboring hydroperoxide groups lead to instability and relatively strong autocatalysis. This work and our own show the difficulty in interpreting other work in the literature on thermally initiated oxidations (mostly at still higher temperatures), where different sequence lengths and different combinations of partly decomposed sequences are responsible for chain initiation.

We think that our own results are most useful in understanding photodegradations of PP near ambient temperatures. Except at the very beginning, these oxidations depend on the photolyses of autoxidation products. Essentially all of these appear to arise from the free radical reactions that we have explored in this report. The work of Adams[25] on the photodegradation of PP in a Weather-Ometer for 72 hours at 35° suggests that continuous photolysis of hydroperoxides, aldehydes, and ketones keeps their concentrations at a low level, and that the groups that accumulate are the photochemically stable ones: alcohol, ester including lactone, acid, and vinyl. Much of the ester comes from esterification of alcohol groups (from hydroperoxides and alkoxy radicals); the vinyl groups arise from the Norrish II cleavage of ketones. After 72 hours, the number average molecular eight of one sample had decreased from 72,000 to 35,000 and the polymer had lost its resistance to flexing.

Our present work shows the proportions of major primary products formed in the chain and nonchain portions of the early oxidation. These

(25) J. H. Adams, J. Polym. Sci. A-1, 8, 1279 (1970).

include P_2O_2 units, which must be both intermolecular (crosslinks) and intramolecular (rings), which are also photolytically unstable, and which have apparently not been reported previously. Our work shows that most pairs of initiating radicals produce P_2O_2, alcohol, aldehyde, ketone, and cleavage in nonchain cage reactions where antioxidants do not interfere, and where they can photolyze and initiate still more radical pairs. Although cleavage and crosslinking are about in balance in the overall reaction in the dark, cleavage predominates in the light. That photooxidation does not cause a greater loss in physical properties may be due to its partial localization, i.e., formation of sequences of hydroperoxides and further oxidation near a previously oxidized site.

Chain propagation outside the initial cage to give PO_2H is apparently readily controlled by added antioxidant. The practical problem in light staoilization is to prevent self-perpetuating photolyses through uninhibitable cage reactions. Light screens and quenchers of photoexcited groups are known and partly effective. Our work may provide an improved basis for separating the possible multiple functions of some additives, such as the initiating and inhibiting properties of antioxidants, and thus lead to improved stabilization. However, at this writing, the most promising new approach to improved stabilization of PP in the light or at elevated service temperatures is to offset the inevitable chain cleavage reactions with a built-in and controlled crosslinking reaction, by copolymerization or use of additives or both.

By separating the oxidation of PP into reactions that are first order and half order in rate of radical production, and by indicating the products of each, our work provides a basis for more meaningful accelerated tests. The failure of a polymer on aging often depends on the net result of several reactions having different dependences on rate of radical formation or energy input and on temperature. It now seems feasible to develop tests that will determine quickly the effects of

40

additives on individual reactions associated with failure. It is also clear why accelerated tests for unknown mixtures of reactions are unpromising.

9.   EXPERIMENTAL

9.1.   Polypropylenes

Most of our experiments were carried out with fractions of a sample of atactic PP, kindly supplied by Dr. H. M. Khelgatian of the Avisun Corporation; the PP was purified and fractionated as follows. About 1060 g of nearly colorless PP, stabilized with a phenolic anti-oxidant, was first separated into fractions that were soluble (assumed to be mostly atactic) and insoluble (partly isotactic) in 1500 g heptane at room temperature. About 1000 g of pentane containing about 180 g of soluble PP was washed with several portions of 2% alcoholic KOH solution until the alcohol layer was no longer colored, to remove stabilizer, and then washed with 1 $\underline{M}$ aq HCl to remove any metals. Thus, 172 g of atactic PP was obtained from an initial 1060 g materials, 165.1 g of which was fractionated as follows.

For fractionation of this soluble PP, benzene and methanol were chosen as solvent and precipitant, respectively. However, the separation resembled more an extraction of low molecular weight PP than a precipitation of a small amount of high molecular weight PP. When methanol was slowly added to the PP solution at room temperature, the high molecular weight fraction appeared in the upper layer and the low molecular weight fraction was in the larger bottom layer. Further treatment of the polymer with methanol gave several additional fractions, all of which were dried to a constant weight in vacuo at room temperature.

Purification and fractionation of PP described above were carried out mostly at low light levels, under an atmosphere that was mostly

41

nitrogen, and at or below room temperature. As a control, deterioration of PP was checked by following the viscosity of its benzene solution in the dark, at room temperature, and in air. No noticeable viscosity change was observed over a period of three weeks.

The results of fractionation are summarized in Table X. PP fraction 1, with the highest molecular weight, was obtained by repeated treatments with methanol and final precipitation by adding the top layer into methanol. The intrinsic viscosities $[\eta]$ of PP before fractionation and PP fraction 11 were determined from their specific and relative viscosities at different concentrations. The intrinsic viscosities of other fractions were calculated by one-point measurement using the Huggins equation in the form

$$[\eta] = [(1 + 4k'\eta_{sp})^{1/2} - 1]/2k'C \tag{31}$$

with $k' = 0.408$ and C in g PP/100 cc solvent. The Huggins constant, k', depends on polymer, solvent, and temperature. Number-average molecular weights $(\overline{M}_n)$ were calculated from intrinsic viscosity by the relation

$$[\eta] = K\,\overline{M}_n^{a} \tag{32}$$

with $K = 2.70 \times 10^{-4}$ and $\underline{a} = 0.71$.[26]

The low molecular weight fraction was viscous and gummy but did not flow at room temperature. The high molecular weight atactic PP was tough.

The infrared spectrum of the purified PP obtained little absorption at 997/cm but strong absorption at 975/cm, indicating that little isotactic PP was present.[27]

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(26) J. B. Kinsinger and R. E. Hughes, J. Phys. Chem., 63, 2002 (1959). Although use of this equation assumes normal molecular weight distributions, which we do not have, we think that it still gives us useful semiquantitative measures of changes in $\overline{M}_n$.

(27) J. P. Luongo, J. Appl. Poly. Sci., 3, 302 (1960).

Table X

FRACTIONATION OF AVISUN ATACTIC PROPYLENE

Fraction No.[a]	Wt. Dry PP g	C_6H_6 $[\eta]$ at 35^0 $\ell/10g$	$\overline{M}_n$[b]
Unfractionated	165.1	0.0235	13800
1	36.5	0.457	35300
1C	27[c]	0.502	41200
1D	4.2[c]	0.414	30600
1B	3.1[c]	0.344	2350
2	~ 1	--	--
3	4.2	0.222	12700
4	4.4	0.258	15800
5	8.4	0.174	9060
6	1.7	0.0767	2850
7	4.6	0.294	18900
8	6.8	0.205	11400
9	7.9	0.0993	4100
10	19.9	0.241	14300
11	18.0	0.195	10650
12	6.0	0.155	7670
13	11.8	0.139	6650
14	36.2	0.0772	2880

[a] Brackets indicate main cuts that were separated further

[b] By equation (32).

[c] By refractionation of 35 g of Fraction 1.

43

The PP-N mentioned in Section 5.2 was prepared at SRI by Dr. D. B. Miller using the method of Natta et al.[28] except that triethylaluminum was used instead of trihexylaluminum and that cyclohexane was used as solvent. The ether-soluble portion had a broad molecular weight distribution, $\overline{M}_w \sim 500,000$ by light scattering and $\overline{M}_n$ about 20,000 by membrane osmometry.

9.2.   Experimental Methods in Absence of Oxygen

9.2.1.   Incorporation and Analysis of DBPO. The toughness of PP and the instability of DBPO necessitated the use for blending purposes of a solvent that can be removed at low temperature. In general, PP was first weighed into the reaction vessel and dissolved in a solvent. The solid DBPO was weighed in by difference from another container, and a weighed amount of Pyrex glass wool was usually added. This glass wool was previously washed successively with acetone, hot N/10 NaOH, M/10 aq ethylenediaminetetraacetic acid (EDTA) and water, and finally dried in vacuo at room temperature. The solvent was then removed in vacuo at 0^0. By weight change, no loss of DBPO was observed under the conditions employed in this work (but significant losses were observed from ethylene-propylene copolymer[2]). The vessel was then immersed in a 45^0 bath. After reaction (usually after 10 or more half-lives of DBPO) the vessel was cooled to -78^0 (to avoid loss of DBPO decomposition products), opened, and after addition of 10 ml of solvent, connected to a vacuum line. The solvent and the decomposition products from DBPO were then transferred in vacuo during about 5 hours, first below 0^0 and finally at 60^0, into a trap cooled with liquid nitrogen. The products were analyzed by glc on a $1/4 \times 12$-ft column of Carbowax 20M on Chromosorb P using benzene as internal standard. Tests of the methods are described in Section 9.2.3.

(28) G. Natta, G. Mazzani, A. Valvassori, G. Sartori, and G. S. Barbagallo, J. Polym. Sci., 51, 429 (1961).

44

9.2.2. Solvent Removal. The solvent used to incorporate DBPO into PP must be removed thoroughly because a small amount of retained solvent markedly affects the behavior of radicals in the PP. At first we thought that a low boiling solvent would be removed easily and completely at 0° at a pressure of 10^{-4} torr or less, but it was not; none of the solvents, benzene, n-pentene, ether, isopentane, fluoro-trichloromethane, or neopentane, could be removed to a level below 5% in 4 hours.

Dispersal of PP on glass wool facilitated solvent removal, and all but $0.7 \sim 0.8$% of pentane (on PP) could be removed in 2 hours at 10^{-5} torr and 0° (Table XI). Further loss of pentane was very slow. The glass wool also provided excellent dispersion of PP and access of O_2 in other experiments. In its absence, film thickness was uneven.

Table XI

REMOVAL OF 6 g OF PENTANE FROM PP AT 10^{-5} TORR AND 0°

No.	PP (g)	Glass Wool (g)	Solvent remaining after various times: wt % on PP or (mg)				
			0.5 hr	1 hr	1.5 hr	2 hr	3 hr
1	0	1.0541	(0.0)	(0.2)			
2	0.4397	1.2956	4.3 (18.7)	2.0 (8.8)	1.3 (5.4)	0.70 (3.1)	
3[a]	0.4063	1.1825	3.4 (14.0)	2.0 (8.0)	1.2 (4.7)	0.79 (3.2)	0.59 (2.4)

[a]With 100-ml round bottom flask.

9.2.3. Recovery on DBPO Decomposition Products from PP. Quantitative recoveries of decomposition products from DBPO are necessary for the measurement of efficiency of initiation. However, some t-BuO· groups were always missing when DBPO was decomposed in PP. To determine whether the low recoveries were due to experimental error, we carried out the

recoveries by the procedures in Section 9.2.1 and found them to be quanti-
tative. For example, from a 10-ml pentane solution containing, respec-
tively, 346.0, 18.91, 17.61, and 18.95 mg of PP, di-t-butyl peroxide,
acetone, and t-butyl alcohol in the presence of approximately 1 g glass
wool, we recovered 18.72, 17.67, and 18.94 mg of the last three products.
In the first few experiments in which the flask was not heated to 60°,
the recoveries of the products, especially of di-t-butyl peroxide, were
not quantitative. In another example, a benzene solution of 9.58 mg of
$t-Bu_2O_2$, 12.7 mg of acetone, and 9.68 mg of t-butyl alcohol was used to
dissolve 0.3838 g of polypropylene without glass wool. Removal of benzene
and decomposition products led to recovery of 9.50 mg $t-Bu_2O_2$, 12.6 mg
acetone, and 9.62 mg t-butyl alcohol, or about 99% of each product.
Therefore, we concluded that the missing t-BuO· groups were bound to the
polymer chain as ether groups.

To test this conclusion, we determined t-butyl ether groups chem-
ically. After the usual recovery of volatile products, the residue was
again dissolved in benzene, saturated with HCl gas, and allowed to stand
overnight at room temperature. The volatile products were again trans-
ferred into the trap under vacuum and analyzed for t-butyl chloride by
glc on the same column. t-Butyl chloride was found, corresponding to 97%
of the missing t-BuO· groups as determined by difference. Thus, essen-
tially all the missing t-BuO· groups were in t-butyl ether groups bound
to PP. However, these recoveries are probably better than the average
of some other experiments.

9.3.   Experimental Methods in Presence of Oxygen

Experiments under oxygen were carried out in sealed tubes to
exhaustion (about ten half-lives) of DBPO. These experiments were simi-
lar to those under nitrogen, but oxygen was added initially and determined
finally with a toeppler pump. A break seal was required for the latter de-
terminations. Except as noted otherwise, PP fraction 11 was used.

Recognizing the advantages of following oxygen absorption continuously during an oxidation, we first tried to follow pressure changes in a constant volume apparatus, but we soon abandoned this effort. First, the low efficiency of initiation and the short kinetic chain length made oxygen absorption small compared with CO_2 evolution from DBPO. Second, the $t-Bu_2O_2$ and t-BuOH formed from DBPO have vapor pressures of 83 and 134 torr at 45° and are slowly and partially vaporized in quantities comparable to the oxygen absorbed. Efforts to follow oxygen absorption continuously from the differences in pressure changes between similar experiments under oxygen and nitrogen give erratic and unreliable results.

9.4.   Determination of Functional Groups

For determination of functional groups, PP was recovered from glass wool by soaking in benzene for 2 days in the dark at room temperature. Benzene was then removed from the frozen PP solution, first at 0°, and finally at room temperature. For example, from 0.4300 g of PP dispersed on 1.1038 g of glass wool in a 50-ml round bottom flask, 0.4306 g of PP was recovered (100.1%). Five hours' soaking resulted in only 85 to 90% recovery.

Hydroperoxides were determined by iodometric titration of a benzene solution of about 50 mg PP according to Hiatt's method[29] with a 10-min reflux; the peroxide content does not increase further with longer refluxing time.

Dialkyl peroxides were determined by the Mair and Graupner Method I^{30} but with added hydrochloric acid. Since this method determines both PO_2H and P_2O_2, a separate PO_2H determination is required. Glacial acetic acid (25 ml) is refluxed for 15 min to reduce the blank.

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(29)   R. Hiatt and W.M.J. Strachan, J. Org. Chem., **28**, 1894 (1963).

(30)   R. D. Mair and A. J. Graupner, Anal. Chem., **36**, 194 (1954).

After cooling, 3g NaI is dissolved and 5 ml of a xylene solution of about 50 mg oxidized PP is added to the mixture; 1 ml of 37% HCl is then added, and the mixture is immediately heated to boiling under a reflux condenser. After 15 min refluxing, 50 ml of water is added through the condenser, and the liberated iodine is titrated with an aqueous solution of 0.1 N $Na_2S_2O_3$. This procedure was carried out under nitrogen to avoid the interference of oxygen from air. The nitrogen flow was cut off during heating to avoid losses of I_2 and resumed when heating stopped. The top of the condenser was closed with a valve to prevent air from diffusing to the refluxing mixture. Tests show that $t-Bu_2O_2$ is quantitatively reduced in only 5 min and liberates 1 mole of iodine per mole of peroxide. With the oxidized polymer, complete reduction is achieved in 15 min with no further liberation of iodine with increasing refluxing time. Blank experiments were run simultaneously with the original PP in a xylene solution; the blanks were about 10% of the determined peroxide ($PO_2H + P_2O_2$) contents.

Aldehydes and ketones were characterized by infrared spectroscopy (band at 1720/cm) using a 25% solution of PP in carbon disulfide. The extinction coefficient was measured using 2-octanone, 10-nonadecanone, and heptanol as model compounds.

The amount of alcohol was determined by infrared spectroscopy by subtracting from the absorption of the peak at 3380/cm the corresponding absorption of hydroperoxides, using t-amyl alcohol and $t-AmO_2H$ as model compounds. Figure 7 shows how the weak absorptions of these compounds at low concentrations, particularly of alcohol, make difficult the determination of alcohol by difference.

The hydroperoxide absorption at 3380/cm is associated with hydrogen-bonded OH groups; it was unaffected by dilution.[31] Free OH was not detected in any oxidized sample.

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(31)   J.C.W. Chien, E. J. Vandenberg, and H. Jabloner, J. Polym. Sci. A-1, 6, 381 (1968).
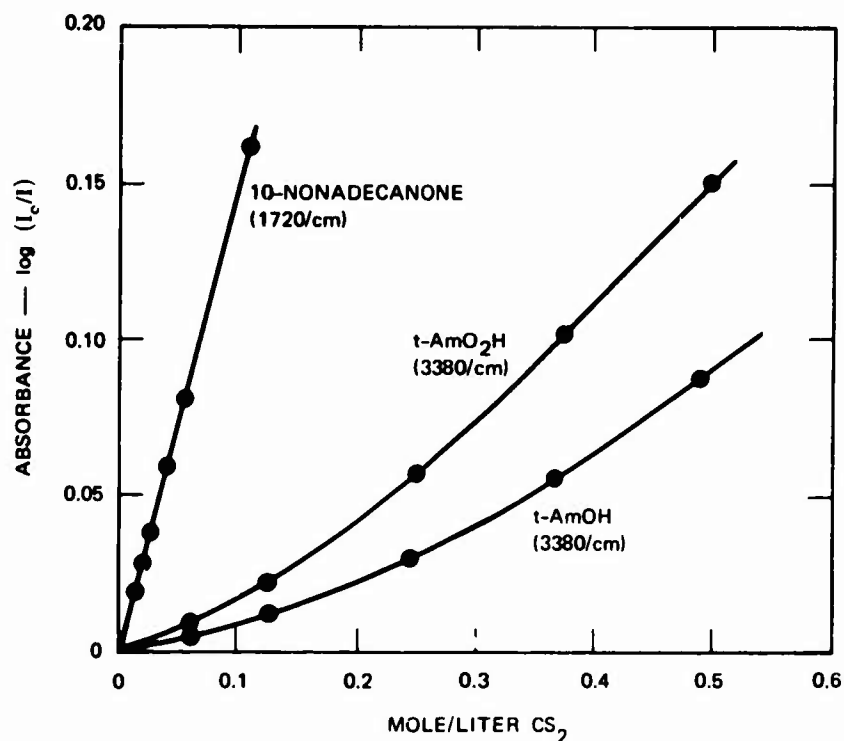
FIGURE 7 CALIBRATION CURVES FOR IR ABSORPTIONS OF KETONE
AND ALCOHOL GROUPS

10. ACKNOWLEDGEMENTS

11.   SIGNIFICANT MATERIAL IN REPORT NO. 8 THAT IS OMITTED FROM THIS
        REPORT

        Report No. 8, the Draft Final Report of January 20, 1971, was
intended to include all our material of some permanent value on peroxide-
initiated oxidations of APP. Since the present report is intended to
approximate a journal publication, some of the material in Report 8,
listed below, is omitted here because it seems unsuitable for that purpose.

        Section 4.   Preliminary decompositions of DBPO in solvents and
                     polymer solutions, from Report No. 1.

        Section 5.1.   Preparation and properties of the little used PP-N.

        Section 5.2.   Details of fractionation of APP.

        Section 5.3.2.   Details of pentane removal from APP.

        Section 5.4.   Some details of DBPO decomposition rate (Table IV
                       and Figure 2).

        Section 6.9.   Gel permeation chromatogram of APP before and after
                       oxidation (Figure 6).

        Section 8.   This section on practical implications of this research
                     is partly superseded or unsuitable for publication.

        Section 10.   Lists critical reviews of journal articles that
                      appeared in Reports 2, 3, and 7.